

①



Eur päisches Patentamt
European Patent Office
Office européen des brevets

① Publication number:

0 133 963
A2

②

EUROPEAN PATENT APPLICATION

② Application number: **84108907.1**

⑤ Int. Cl.: **A 61 K 7/021**

② Date of filing: **27.07.84**

③ Priority: **29.07.83 US 518498**

④ Date of publication of application: **13.03.85**
Bulletin 85/11

⑥ Designated Contracting States: **AT BE CH DE FR GB IT**
LI LU NL SE

⑦ Applicant: **Revlon, Inc., 767 Fifth Avenue, New York,**
N.Y.10022 (US)

⑦ Inventor: **Tietjen, Marlene, 140 Seventh Avenue, New**
York New York (US)
Inventor: **Brown, Ivonne, 36 Westbrook Lane, Roosevelt**
New York (US)
Inventor: **Macchio, Ralph A., 17 Columbine Court,**
Middletown New York (US)

⑦ Representative: **Körber, Wolfhart, Dr. et al,**
Patentanwälte Dipl.-Ing. H. Mitscherlich Dipl.-Ing. K.
Gunschmann Dr.rer.nat. W. Körber Dipl.Ing. J.
Schmidt-Evers Dipl.-Ing. W. Melzer Steinsdorfstrasse 10,
D-8000 München 22 (DE)

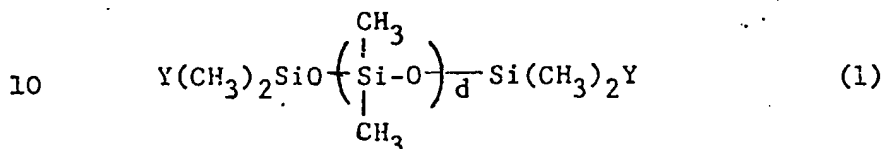
⑥ **Silicone-based cosmetic products containing pigment.**

⑦ Unexpectedly high amounts of pigment can be incorporated in anhydrous, pigmented cosmetic compositions containing an organically substituted polysiloxane by providing the pigment in a hydrophobic silicone coating.

EP 0 133 963 A2

1 SILICONE - BASED COSMETIC PRODUCTS CONTAINING PIGMENT

This invention relates to pigmented cosmetic products in stick, cake, or cream form such as eyeshadows, foundations, moisturizers, and skin protectants. More specifically, the invention relates to such cosmetic products which contain a silicone base, e.g. dimethylpolysiloxane fluid. This fluid has the chemical formula



wherein both Y substituents are $-CH_3$, or both are $-OH$, and in which the degree of polymerization d is a value, typically between 1 and 150, effective to give the fluid a viscosity of 0.65 to 1 million centistokes at $25^\circ C$. (Viscosity of such fluids can be measured by widely recognized test methods, such as the spinning cup test.)

Although dimethylpolysiloxane and other silicone fluids offer the properties of water repellency, slip, non-greasy emollience, and low penetration of the skin, their use in anhydrous pigmented cream, cake and stick products is limited by the difficulty of dispersing inorganic pigments in the silicone base. The result is that such products contain only small amounts of pigment, or contain pigment which forms uneven color streaks in the final product.

It is therefore highly desirable to incorporate inorganic cosmetic pigments readily into a cosmetic product which contains a silicone fluid or a mixture of such fluids.

The invention comprises anhydrous, pigmented cosmetic products comprising a base of dimethylpolysiloxane having formula (1) above or mixtures of dimethylpolysiloxane

1 with the organo-polysiloxanes having formula (2), (3),
or (4) given below, or mixtures thereof, in which the
pigment is easily dispersed and remains uniformly dis-
tributed without separating or segregating even at the
5 unusually high pigment contents of 40 to 60 wt. %.

The more dispersible pigment comprises hydro-
phobic, finely divided particles of inorganic pigment
whose surface is chemically bonded to, and physically
completely coated by, polysiloxane.

10 By "more dispersible" we mean that by comparison
to the same pigment in uncoated form, the coated pigment
is dispersed uniformly throughout the cosmetic composition
more easily and quickly during formulation of the com-
position, and it stays dispersed instead of settling or
15 segregating out of the composition.

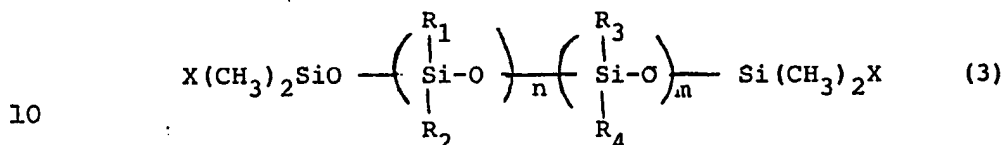
Cosmetic compositions in accordance with this
invention can contain a total of 10 to 70 wt. % of
silicone compounds having formula (1). Alternatively, the
compositions contain 10 to 70 wt. % of a combination of
20 compound (1) and one or more compounds having formulas
(2), (3), or (4), provided that at least 10 wt. % of the
composition is dimethylpolysiloxane of formula (1). The
other silicone compounds, any one, two, or three of which
are included with the dimethylpolysiloxane, can be in-
25 cluded in any amount provided that the total of silicones
(1) - (4) is up to about 70 wt. % and provided that the
combination of those compounds is a stable, homogeneous
one-phase mixture at room temperature (25°C). The pre-
ferred range of the total amount of compounds of formulas
30 (1) - (4) is 20 - 50 wt. %, in which case dimethylpoly-
siloxane comprises at least 20 wt. % of the composition.

1 Formula (2) is an organosilane:



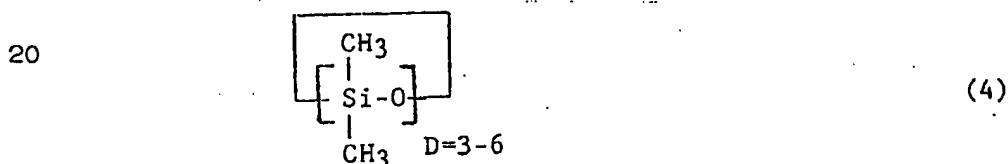
5 wherein R is alkyl having 1 to 30 carbon atoms, or aryl.

Formula (3) is an organo-polysiloxane:



10 wherein R_1 and R_3 are independently alkyl having 1 to 30 carbon atoms or aryl; X is alkyl or alkyl-oxy and has 1 to 30 carbon atoms; R_2 is alkyl having 2 to 30 carbon atoms, aryl, or trimethylsiloxy ($(\text{CH}_3)_3\text{SiO}-$);
 15 R_4 is alkyl having 1 to 30 carbon atoms, or aryl; n is 1 to 100; m is 0 to 100; and (n plus m) is 1 to 100.

Formula (4) is cyclomethicone:



20 As used herein, "alkyl" and the alkyl moiety of alkyl-oxy includes straight- and branched-chain aliphatic groups containing 1 to 30 carbon atoms; examples include methyl, ethyl, octyl, and octadecyl. Preferred aryl groups include phenyl and groups in which a phenyl ring is connected to the Si by an alkyl or alkylene bridge
 25 up to 3 carbon atoms long, such as styryl.
 30

1 Preferred dimethylpolysiloxanes of formula (1)
have a viscosity of about 5 to about 500 centistokes
(abbreviated herein as "cs").

Examples of organo-polysiloxanes of formula (3)
5 where m equals zero are polymethyloctyl-siloxane, poly-
methyloctadecyl-siloxane, polyphenyltrimethylsiloxy-
siloxane, polymethylphenyl-siloxane, and octadecyloxy-
dimethylpolydimethyl-siloxane. Examples where n and m
are both non-zero include polymethyl/polymethylphenyl-
10 siloxane, polymethylstyryl/polymethylethyl-siloxane,
and polymethylstyryl/polymethyldodecyl-siloxane. In
this nomenclature, the one or two substituents named
after "poly" are each attached to the silicon atom in
each repeating unit, and substituents before "poly"
15 are attached to both ends of the polymer chain. To
illustrate, "polymethyloctyl-siloxane" is a compound
of formula (3) in which m is zero, R_1 is methyl, and R_2
is octyl. Furthermore, the term "polymethylstyryl/
polymethyldodecyl-siloxane" means a compound of formula
20 (3) wherein R_1 is methyl, R_2 is styryl (e.g. $C_6H_5CH:CH-$),
 R_3 is methyl, and R_4 is dodecyl (e.g. $C_{12}H_{25}-$).

The cosmetic composition can also contain 4 to
20 wt. % and preferably 6 to 15 wt. % of a cosmetically
acceptable wax; those of ordinary skill in this art
25 will readily identify what is meant by this term.

Examples are carnauba, ozokerite, glyceryl tribehenate,
beeswax, candelilla, paraffin, bayberry wax, lanolin,
micro-crystalline wax, montan, rice wax, mono-, di-, and
triglycerol esters of C_{12} - C_{36} fatty acids, polyethylene,
30 polyethylene/polyvinyl acetate copolymers, polyethylene/
polyacrylic acid copolymers, C_{12} - C_{36} fatty alcohols, and

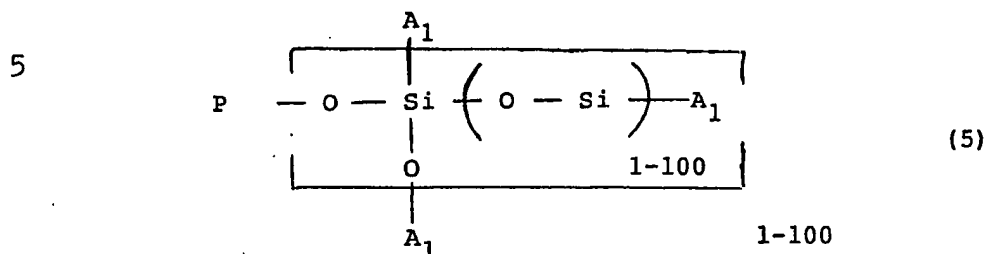
1 C_{12} - C_{36} fatty alcohol esters of C_{12} - C_{36} fatty acids,
provided that the wax is solid at room temperature (25°C).
The waxes are further characterized in that they have
crystalline to microcrystalline structure; leave a film
5 when applied to the skin from a cosmetic stick or cream;
have low viscosity just above their melting points; and
exhibit low solubility at room temperature in the dimethyl-
polysiloxane described hereinabove. Typically the waxes
are high-molecular-weight hydrocarbons (C_{12} - C_{100}) or
10 mixtures thereof, and esters of high-molecular-weight
(C_{12} - C_{36}) fatty acids with high molecular-weight (C_{12} - C_{36})
fatty alcohols, and mono-, di-, or triesters of C_{12} - C_{36}
fatty acids with glycerol.

If the cosmetic composition contains wax, it
15 should contain enough of an organo-polysiloxane of
formula (3) described above to provide that the com-
position, whether it is a stick, a cake, or a cream,
is a single homogeneous phase. That is, above the
melting point of the highest-melting ingredient one
20 should be able to stir together a molten mixture of the
three components (dimethylpolysiloxane, organo-polysiloxane,
and wax) easily using conventional mixing equipment; and
then, on discontinuing stirring, the components should
not separate into discrete layers or areas of different
25 composition. Likewise, when a stirred, molten mixture
of the three components is cooled to 25°C, the cooled
product should remain one continuous phase and the wax
should not ooze, bleed, or otherwise separate from the
siloxane and/or silane components. In general, the proper
30 relative amounts of wax and the two silicone components
can readily be determined by examination of the behavior

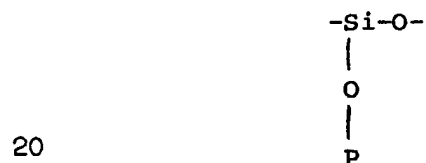
1 of a sample formulation; as a general guide to formulations
known to be successful, the weight percentage of the wax
can be up to about one-third of the combined weight
percentage of the silicone components, and the weight
5 ratio of organo-polysiloxane (3) to dimethylpolysiloxane
can be up to about 1:1. Variations from these figures
are also contemplated within the broad aspect of the
present invention, however, so long as the proportions
chosen permit the creation of a physically stable one-
10 phase cosmetic product. Further disclosure regarding
this invention is contained in another application filed
on even date herewith entitled "One-Phase Silicone-
Based Cosmetic Products Containing Wax" filed by
Marlene Tietjen, Jane Hollenberg, and Richard Rigg
15 (under applicant's docket number REV 83-3/A) and as-
signed to the assignee of this application. The dis-
closure of that application is hereby incorporated
herein by reference.

The anhydrous cosmetic composition of this
20 invention also contains pigment which remains uni-
formly dispersed in the silicone better than has
heretofore been known. The coated pigment is charac-
terized by its complete hydrophobicity. That is, it
is impossible to suspend or disperse even a very
25 small amount of the coated pigment in water. The
coating does not affect the color; the coated pigment
exhibits the same color as the uncoated pigment. The
coating is polysiloxane which is chemically bonded to
the pigment; it is believed to be bonded through oxygen
30 atoms to the surface of the pigment.

1 The coated pigment can exhibit structural formula
(5)



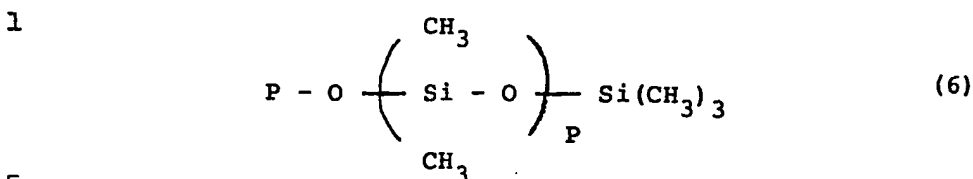
wherein each of the oxygen atoms at the left end of formula
(5) is attached to an atom P in the pigment surface; and
A₁ is an alkyl or alkenyl group having up to 30 carbon
atoms. A number of adjacent polysiloxane chains as shown
15 in (5) can be cross-linked through oxygen atoms to form
a polysiloxane chain with up to 100 repeating



units that extends along the pigment surface, in addition
to the polysiloxane chain which extends away from the
pigment surface. Examples of alkyl groups are methyl,
ethyl, octyl, and octadecyl. "Alkenyl" includes carbon
25 chains with more than one double bond; examples of alkenyl
groups include ethylene, propylene, acrylyl, methacrylyl,
and residues of unsaturated fatty acids such as oleic
(e.g. C₁₇H₃₃⁻), linoleic (C₁₇H₃₁⁻), and linolenic (C₁₇H₂₉⁻).

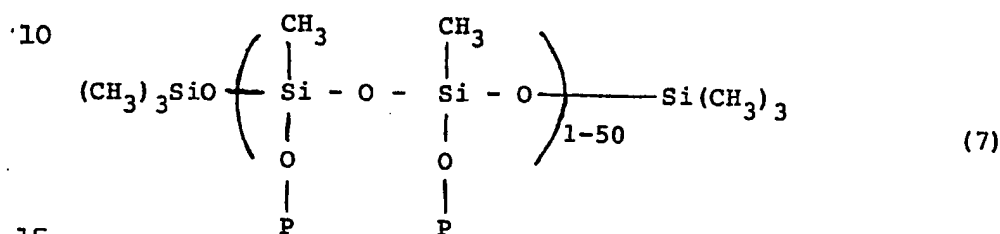
30 The coated pigment can also exhibit structural
formula (6)

35



5 wherein p is 1 - 100, and P is an atom in the pigment surface.

The coated pigment can also exhibit structural formula (7)



wherein P is an atom in the pigment surface, and in which each of the up to 100 repeating (Si-O) units is bonded through an oxygen atom to the pigment surface.

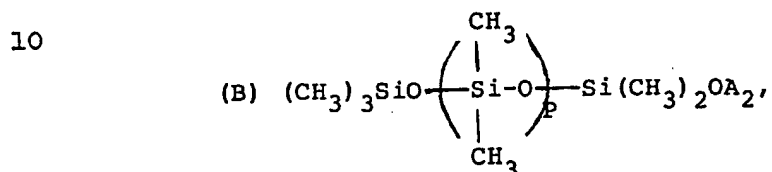
The number of polysiloxane chains of formulas (5), (6), and (7) that are bonded to the pigment surface is not known but is sufficiently high to coat the pigment completely and render it completely hydrophobic; hydrophobicity can readily be determined by placing the coated pigment into water and observing whether any becomes dispersed or suspended in the water.

Suitable pigments include all inorganic pigments which are usable in cosmetic formulations.

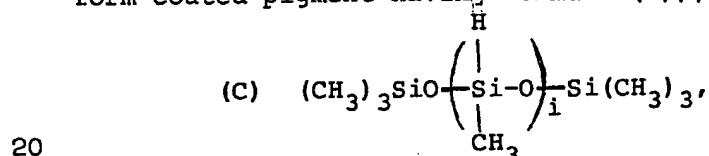
Particular examples include talc, mica, titanium dioxide, iron oxide, kaolin, ultramarine, chromium oxide, chromium hydroxide, zinc oxide, silica, manganese violet, and their equivalents.

1 The pigment (or a mixture of two or more pig-
 2 ments) can be coated by placing it in dry, finely divided
 3 form in a mixer and adding a silicone material selected
 4 from the group consisting of

5 (A) $A_1SiX_1X_2X_3$, wherein A_1 is an alkyl or
 6 alkenyl group having 1 to 30 carbon atoms, and X_1 , X_2 ,
 7 and X_3 are independently chloro, methoxy, or ethoxy
 8 (this material will form coated pigment having formula
 9 (5));



11 wherein p is 1 to 100 and A_2 is hydrogen or an alkyl
 12 group having 1 to 30 carbon atoms (this material will
 13 form coated pigment having formula (6));



16 wherein i is 1 to 100 (this material will form coated
 17 pigment having formula (7)); or a one-phase mixture of
 18 two or all three of A, B, and C. The relative amounts
 19 of fluid: pigment should be sufficient to coat the
 20 pigment particles; generally a fluid: pigment weight
 21 ratio is satisfactory for which 1 - 4 wt. % of the
 22 final product is silicone. The pigment and fluid are
 23 intimately mixed thoroughly to obtain a uniform dis-
 24 ~~persion of the fluid on the pigment, in which the fluid~~
 25 completely coats the particles of pigment. The slurring
 26 operation is advantageously carried out at a temperature

1 of 25°C to 160°C effective to promote hydrolysis and
reaction of the silicone with the pigment. As an
alternative to synthesis, satisfactory coated pigments
usable in this invention are sold in a wide variety of
5 shades by Whittaker, Clark & Daniels, Inc., doing
business as Clarks Colors; the product has the trade
name Hydrophobes.

To make the cosmetic composition of the
invention, one stirs the dimethylpolysiloxane component
10 (1) with any other liquid components (such as silicone
component (2), (3), and/or (4) if liquid at room tem-
perature) to achieve a uniform mixture. Any of the
components which are initially dry (such as fillers,
preservatives, and pigments, including the coated pig-
15 ments described herein) are then added to the liquid
mixture and dispersed using high shear equipment (such
as a 3-roll mixer or Kady mill) until a homogeneous
dispersion is obtained. This dispersion is then heated
to a point above the melting temperature of the wax
20 material which is to be added (usually 60-95°C). The
wax, and any silicone component which is solid at room
temperature, are added and stirred with a high-shear
mixer until all components are melted and dispersed
uniformly. The melted mixture is poured hot (at 60-95°C)
25 into the containers of choice, e.g. pans, jars, or sticks.

The resulting product can be used per se as a
cosmetic which is applied to soothe and moisturize the
skin. One can also add optional ingredients such as
cosmetically acceptable fillers, preservatives, and/or
30 fragrance. Dry ingredients are added in finely divided
form to the molten mixture, with stirring, before the

1 mixture is poured into containers. Examples of fillers
(added alone or in combination) are talc, mica, nylon,
silica, kaolin, zinc oxide, magnesium silicate, calcium
silicate, calcium carbonate, and equivalent materials,
5 added in amounts up to about 35% by weight of the final
product. Another feature of the present invention is
that the filler(s) can also be silicone-coated in the
same manner as the pigments described herein. Examples
of preservatives are methyl and propyl parabens, and
10 equivalents thereof, in amounts up to about 0.5 wt. %.
The cosmetic formulator will recognize that any of the
well-known blends of fragrance oils conventionally sold
by fragrance manufacturers can be added, in amounts
generally ranging up to about 0.5 wt %.

15 The composition can contain up to about 20 wt. %
of one or more cosmetically acceptable oils, to further
augment the feel of the product on the skin and to
adjust the product's consistency. Suitable oils are
glycerol esters and C_3 - C_{22} alcohol esters of C_3 - C_{22}
20 fatty acids, and C_{12} - C_{22} fatty alcohols, provided that
they are liquid at 25°C and form homogeneous mixtures
with the cosmetic composition. A preferred example is
2-ethyl-1-hexyl palmitate. The ordinarily skilled
formulator will recognize that other compounds known to
25 be equivalent to those listed herein can be incorporated
into the composition of this invention.

Utilization of this discovery renders the pig-
ment easily dispersible in the formulation. The dis-
covery also permits the preparation of products in which
30 the pigment remains uniformly dispersed without separation.
These properties are particularly advantageous at pigment

1 contents over about 10 wt. % and even more so when the
pigment content is over 40 wt. %, e.g. 40-60 wt. %.
Satisfactory pigmented products with such high pigment
5 contents were previously thought impractical or unobtain-
able because of the difficulty of dispersing such a high
amount of pigment in the oily base. This development is
particularly unexpected in view of the knowledge that
pigments do not disperse well in silicone- based oils.
By "pigment" we mean to include a pigment composition
10 which is made by intimately blending amounts of two
or more other unblended pigments.

Utilization of the coated pigment allows
incorporation of more pigment (generally about 10 -
20% more) into an anhydrous cosmetic composition than
15 is otherwise attainable. The higher pigment level
provides a smooth, dry feeling makeup which has
excellent slip characteristics due to the silicone fluid
base.

The one-phase, anhydrous, pigmented composition
20 preferably contains 40-60 wt. % of the coated pigment.
The balance can comprise the silicone compounds (1) and
(2), (3) and/or (4). Alternatively, the composition can
contain optional cosmetically acceptable filler, fragrance,
oil, and/or wax components. Examples of these components
25 and typically acceptable amounts thereof are listed above.

The coated pigment and other finely divided solid
particles have a size generally no larger than about 50
microns. It will be recognized that materials such as
mica, whose crystalline properties favor formation of
30 flakes, will be finely divided and will be up to about
150 microns in the long dimension.

The invention is further described in the
following Examples.

1 In each Example, all components that are liquid
at 25°C were mixed together at room temperature, and then
the dry ingredients (preservatives, fillers, pigments)
were mixed into the liquid using high-shear equipment.
5 When the resulting mixture was homogeneous and all solid
components were uniformly dispersed, the mixture was
heated to above the melting point of the wax that was
about to be added (or above the highest melting point if
more than one wax was added), and then the wax was added
10 and stirred into the mixture. If the organopolysiloxane
is a solid at 25°C, it was added at the same time as the
wax. The entire mixture was stirred using conventional
equipment (Lightnin brand mixer or Kady brand mill) until
a uniform mixture was obtained. The mixture was poured
15 hot (60-95°C) into its intended package. No phase
separation or component segregation occurred during or
after cooling of the product. All solid ingredients,
including coated pigments, were added in finely divided
form.

20 A foundation was prepared using this procedure
except that the pigments were not coated with any
silicone:

Foundation

25	Glyceryl tribehenate	6.0	
	Polymethyloctadecylsiloxane	6.0	
	2-ethyl-1-hexyl palmitate (oil)	13.0	
	Dimethylpolysiloxane (10 cs)	25.0	
	Pigment		
30	Titanium dioxide	17.0	
	Iron oxide	5.0	
	Talc	15.0	
	Mica	13.0	50.0

35

1 The melt viscosity of the above formulation
was too high to permit it to be poured into containers.
The surface of the product exhibited color striations
and a mottled appearance, which indicated poor dispersion
5 of the pigment in the product. When the pigment components
were provided with a coating having formula (7) prior to
incorporation into the composition, there resulted a
pourable, homogeneous product. The high pigment level
became an advantage rather than a drawback, and provided
10 a smooth, dry feeling product.

Other examples, which were prepared the same
way as above, in which the pigment was coated prior to
addition, were:

Cream Powder Foundation

15		<u>A</u>	<u>B</u>
	Glyceryl tribehenate	6.0	10.0
	Polymethyloctadecyl siloxane	6.0	-
	2-ethyl-1-hexyl palmitate (oil)	13.0	15.0
	Dimethylpolysiloxane (10 cs)	25.0	30.0
20	Pigment*:		
	Titanium dioxide	20.0	14.5
	Iron oxide	7.0	3.0
	Talc	13.0	9.5
	Mica	10.0	18.0

25 * The pigment had been coated with polymethyl hydrogen
siloxane.

1	<u>Eyeshadow</u>	
	Dimethylpolysiloxane	10.0
	Glyceryl tribehenate	6.0
	Candelilla	2.0
5	C ₁₂ -C ₁₅ alkyl benzoate ester	7.0
	Cyclomethicone D=5	30.0
	Bismuth oxychloride	5.0
	Pigment*:	40.0
	Chromium oxide	15.0
10	Ultramarine blue	10.0
	Mica	15.0
* The pigment had been coated with methyl-trimethoxy silane.		

15

20

25

30

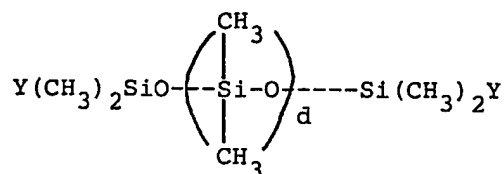
35

1 WHAT IS CLAIMED IS:

5 1. An anhydrous homogeneous pigmented cosmetic product comprising

(a) 10 to 70 wt. % of dimethylpolysiloxane having the formula

10



15

wherein both Y substituents are $-CH_3$, or both are $-OH$; and wherein d is sufficient to impart to the dimethylpolysiloxane a viscosity of 0.65 to 10^6 centistokes at $25^\circ C$ and

20

(b) a coated pigment which comprises finely divided particles of inorganic pigment whose surface is chemically bonded to, and physically completely coated by, a polysiloxane which coating renders the particles hydrophobic; wherein said pigment is readily dispersible in component (a) without settling or segregating.

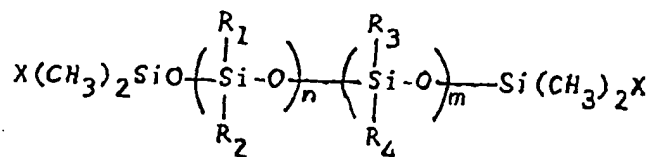
25

2. An anhydrous homogeneous pigmented cosmetic composition
 30 according to claim 1 wherein component (a) may also contain in a one phase mixture

(1) organosilane having the formula $RSi(CH_3)_3$
 wherein R is alkyl having 1 to 30 carbon atoms,
 or aryl;

35

(2) organopolysiloxane having the formula



wherein R_1 and R_3 are independently alkyl having 1 to 30 carbon atoms, or aryl;

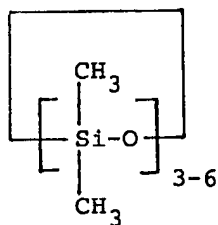
X is alkyl or alkyl-oxy and has 1 to 30 carbon atoms;

R_4 is alkyl having 1 to 30 carbon atoms, or aryl;

R_2 is alkyl having 2 to 30 carbon atoms, aryl, or $-OSi(CH_3)_3$; and

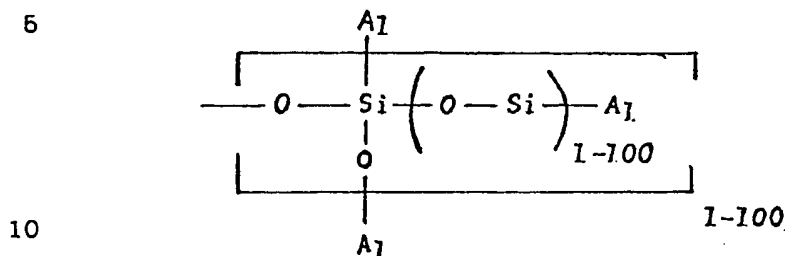
n is 1 to 100, m is 0 to 100, and $(n \text{ plus } m)$ is 1 to 100; or

(3) cyclomethicone having the formula



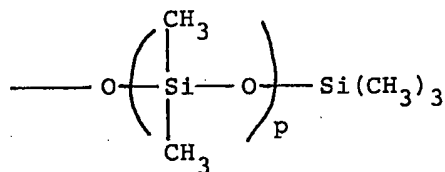
provided that said composition contains at least 10wt. % of component (a).

- 1 3. The composition of claim 1 or 2 wherein said poly-
siloxane coating exhibits the structure

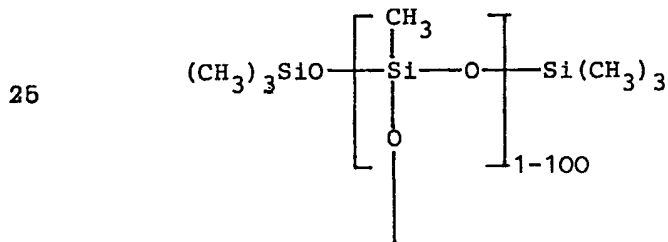


wherein A_1 is an alkyl or alkenyl group having up to
30 carbon atoms; or the structure

15



wherein p is 1 - 100; or the structure



30 wherein there are enough of said chains bonded to each
pigment particle to render the pigment hydrophobic.

4. The composition of claim 1, 2 or 3 wherein said
pigment comprises up to 60 wt. % of the composition.

35

- 1 5. The composition of claims 2 to 4 further comprising
from 4 to 20 wt. % of a cosmetically acceptable wax,
provided that there is a sufficient amount of silicone
component (2) that the product formed by melting said
5 composition and then cooling it to 25°C is a single
homogeneous phase.
6. The composition according to any of the preceding
claims wherein at least one of R₁, R₂, R₃ and R₄ is
10 alkyl.
7. The composition according to any of the preceding
claims wherein the aryl group is phenyl or styryl.
- 15 8. The composition of any of the claims 2 to 7 wherein
(a), (1), (2) and (3) comprise 20 to 50 wt. % of the
total composition, and (a) comprises at least 20 wt. %
of the total composition.
- 20 9. A composition according to claim 2 comprising by
weight about 6 wt. % wax, about 6% polymethyloctadecyl
siloxane, about 13% of cosmetically acceptable oil,
about 25% of dimethylpolysiloxane (10 cs), and about
50% polysiloxane-coated pigment.
25
10. A composition according to claim 2 comprising by
weight about 10% wax, about 15 % cosmetically acceptable
oil, about 30 wt. % dimethylpolysiloxane (10 cs), and
about 45% of a polysiloxane-coated pigment.
30
11. A composition according to claim 2 comprising by
weight about 8% wax, about 7% cosmetically acceptable
oil, about 30% cyclomethicone (D=5), about 5% pigment,
about 40% polysiloxane-coated pigment, and about 10%
35 dimethylpolysiloxane (10 cs).